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Fax to Adams

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**Translation of a Patent description from German language into English**

**Notes:**

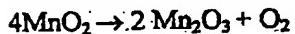
- Additions in [square brackets] were added by the translator for clarity.
- The original German text is full of long sentences with a complicated structure. For clarity, the translator split these sentences into several shorter ones without changing any of the meanings.
- Problems exist with reading the given text due the multiple reproduction and the small text of the original. For example, please note the similarities of the German words Abwesenheit (absence) and Anwesenheit (presence). If the print is bad, it is easy to mix up the letters "b" and "n", which completely changes the meaning.

OS 37 31 889

**Description**

The invention consists of a process to separate Nitrogen-oxides from exhaust gases of fired boilers, combustion engines and from other exhaust-gas-producing installations. Exhaust gases are being fed into a reaction chamber filled with solid Manganese-dioxide in an activated state. This Manganese-dioxide will react with at least one of the existing Nitrogen oxides.

A process of this type is already described in DE-OS 33 12 890. This paper [patent-description?] presents and describes a process to clean exhaust gases from sources listed above by using as reactive media a pile of metal oxides which also might contain Manganese-dioxide-ore ( $MnO_2$ ) [German word is "Braunstein" = brown-stone]. The metal oxides are compressed into pellets of high porosity which will separate the contaminations from the exhaust gases. The paper already mentions, that -depending on the design of the process and the temperature of the arriving exhaust gases- Manganese-dioxide may either be used as direct oxidation-media for Nitrogen-oxides based on the reaction



[The second part of the sentence which should start with an "or" is missing in the original German text or the word "either" should be removed]. Due to the presence ["absence" ?, see notes above] of Oxygen, the Manganese-dioxide is used simply as "go-between" in the sense, that the released Oxygen is immediately being re-absorbed out of the exhaust gases and is used to re-generate Manganese-dioxide-ore. Especially at low gas temperatures Manganese-dioxide-ore will act in a quasi-catalyst type of way and will produce a high Oxygen concentration near the active center of the active media or will act as a "real" catalyst and will accelerate the transformation processes and the oxidation reaction. The context of the paper makes clear, that Manganese-dioxide is being used

exclusively to supply the Oxygen to oxidize NO to NO<sub>2</sub>. The oxidation shall happen in such a way, that in the end equal molar amounts of Nitrogen-oxides are present (NO<sub>2</sub>: NO = 1:1).

Tests indicated, that metal-oxides as described in above paper have generally a very low ability to absorb Nitrogen-oxides. However, Manganese-dioxide at a temperature below 200°C is perfectly suited to absorb NO<sub>2</sub>. In the range of 250°C to 500°C, NO<sub>2</sub> is being released again at a sufficient rate to re-generate the active Manganese-dioxide. However, in a process as described in "Im Stande der Technik" [a trade journal?], the re-generation often produces inactive Mn<sub>2</sub>O<sub>3</sub>, which practically stops the further absorption process. Basically, Manganese-dioxide in form of pellets could be used as absorption material. However, only small absorption rates for Nitrogen-oxides can be observed if the pellets are being produced in traditional ways, since too much active material is being covered by the binding agent. Also, the production cost of pellets of this type is considerable, since the pellets must be re-worked after their use. This means crushing, separating, processing and then re-forming the pellets.

The main challenge can now be described as follows: Modify the above-described processes in such a way (at least the part about reactions with Manganese-dioxide), that the desirable characteristics of the Manganese-dioxide are being utilized in a better way. Use less costly variations of the material and avoid the expensive process to produce pellets.

The challenge can be met in a process, in which Manganese-dioxide is being used to separate Nitrogen-oxides via the following steps:

- a) an oxidizer is being added to the exhaust gases. The two react before the reaction with the Manganese-dioxide and Nitrogen-monoxide (NO) is being oxidized to NO<sub>2</sub>.
- b) in the reaction occurring afterwards, the reacting temperature is kept at 20 - 200°C. During this time, the original and the newly formed NO<sub>2</sub> react with the Manganese-dioxide and produce mainly Manganese-nitrate (Mn(NO<sub>3</sub>)<sub>2</sub>).

The proposed process will work if pure Manganese-dioxide is being used; however, the process will also work if "technically pure" Manganese-dioxide or Manganese-dioxide-ore with a high content of MnO<sub>2</sub> is being used.

The process may either occur in a chamber filled with a loose pile of Manganese-dioxide granulate or pellets or it can be blown into the exhaust gas stream in which the pre-oxidation from NO to NO<sub>2</sub> already has happened [this is not a translating error, the original text truly claims, that the process may be blown into the gas stream]. MnO<sub>2</sub> or ore containing MnO<sub>2</sub> ground into fine dust may be blown directly into the exhaust gas stream. The reaction inside the exhaust gas stream can occur by using identical or opposite directions of flow. The injected material is being carried away by the exhaust gas stream. The reaction to Mn(NO<sub>3</sub>)<sub>2</sub> happens during this time.

It is also possible to flow the exhaust gases crosswise or from the bottom up through a drizzle of slowly falling granulate containing MnO<sub>2</sub>. In this case, the pressure losses of the flowing media are considerably lower than in a reactor with solid material. Below 200°C, MnO<sub>2</sub> will react with NO<sub>2</sub> and form Mn(NO<sub>3</sub>)<sub>2</sub>. The solid particles are being filtered out in suitable dust separators which may be equipped with cyclones, cloth filter elements or similar equipment. A small part of the separated solid material is being removed from the filters and regenerated or it is being sent to an ore-smelter to be processed into metallic Manganese. It is also possible to "peel" the granulate particles after they leave the sieve in the reaction chamber. In this process, the used surface area of the pellets is being removed [peeled] and a fresh surface is being exposed, ready to re-enter the reaction process.

The regeneration process happens simply in such a way, that Mn(NO<sub>3</sub>)<sub>2</sub> is being thermally separated at a temperature above 250°C into NO<sub>2</sub> and into especially active MnO<sub>2</sub>, which can be reused in the process. The separated NO<sub>2</sub> may be used to produce nitric acid or may be split into its benign components N<sub>2</sub> and O<sub>2</sub> by using a catalytic reaction.

Other types of Manganese-oxides which might form during the reaction can also be reduced to Manganese-dioxide through known processes, for example by using Ozone or by first producing Manganese-sulfate.

Examples of possible oxidizers are the Oxygen in the air, Ozone or Hydrogen-peroxide. Of course, mixtures of above oxidizers may be used as well.

The size of the Manganese-dioxide granulates or pellets can be varied to suit the desired size of the reactor, the process time and the available raw material. Generally, granulates or pellets with a size of 2 to 8 mm are being used.

It is a special advantage that the above-described process will operate with Manganese-dioxide in its natural state, which comes from Manganese-dioxide-ore [Braunstein]. It is only necessary to form the raw ore into pellets or granulates. The process is therefore very cost effective. Tests performed indicate that it is possible to remove practically one-hundred percent of the original Nitrogen-oxides found in the exhaust gases listed at the top.

Possible applications of this invention are being explained with examples and a drawing. The drawing shows schematically the two different separation cycles which are possible using the above process (see example 4 and 5).

Fig. 1 shows example 4.

Fig. 2 shows example 5.

#### Example 1

A single home furnace was operated continuously for eight hours on gas fuel. The exhaust gas volume produced was 35 Nm<sup>3</sup>/h (Normal cubic meter per hour) at a temperature of 160 - 190°C. A total of 280 Nm<sup>3</sup> of exhaust gases were therefore produced. The average Nitrogen-oxide content was 70 ppm. The combustion occurred

with above-stoichiometric amounts of air with its natural content of O<sub>2</sub> ( $\lambda = 1.5$ ). The exhaust gases were cooled to 110 - 120°C before entering the reactor.

Technically pure Manganese-dioxide-ore (80% MnO<sub>2</sub> by weight) in a processed form and suitable for active reaction was granulated and separated in such a way that the diameter of the granulate was 2 - 5 mm. 17.9 kg of these granulates was filled into a cylindrical reactor. The Manganese-dioxide-ore granulates filled the reactor to about 2/3 of its volume. The reaction temperature inside the reactor was measured to be 110 - 130°C, equal to the measured exhaust gas temperature. The test reactor was built in such a way, that exhaust gas could be sent through the same Manganese-dioxide filled reactor in a single or in multiple passes. The residual content of Nitrogen oxide after one pass was less than 1 ppm. After two or three passes, the residual NO was less than 1 ppm.

#### Example 2

A single-home, liquid-fueled furnace with a capacity of about 15 kW was operated on heating fuel EL ["Extra Leicht" = Diesel #2]. In an uninterrupted test run, 0.8 kg/h of Diesel #2 were burned which produced an exhaust volume of 35 Nm<sup>3</sup>/h or a total volume of 250 Nm<sup>3</sup> [original text does not specify the operating time]. The exhaust gas temperature was 190°C. The measured Nitrogen oxide content averaged 55 ppm, corresponding to a total amount of Nitrogen oxide of 26.5 g, normalized to the NO<sub>2</sub> content required by "TA Luft" [a German air quality specification].

Before the reaction with Manganese-dioxide, air with the usual amount of Oxygen and laced with 0.1 % of Ozone (O<sub>3</sub>) was added to the exhaust stream [1 Promille = 0.1 Percent]. The overall  $\lambda$  value was again set to 1.5.

3 kg of technically pure Manganese-dioxide-ore [Braunstein] in an active form and a pellet size of 2 - 4 mm were put into a reactor. The material had a MnO<sub>2</sub> content of 50 % by weight and filled a smaller size reactor to about 1/2.

As an average, ten passes through the reactor were used. The cleaning effect of the original Nitrogen oxides was practically 100 %. The final weight increase of the Manganese-dioxide material used was 1.7 % by weight.

[The original description in German does not explain how you can have a continuous operation and still can make ten passes through the same reactor]

#### Example 3

A stationary 4-cylinder internal combustion engine with a cylinder volume of 500 cm<sup>3</sup> [it is not specified if this is the total volume or the volume for each cylinder] was operated for 8 hours at 300 RPM in an uninterrupted test run. Unleaded gasoline with normal octane rating was used. The exhaust gas stream was 90 Nm<sup>3</sup>/h, which means a total exhaust volume of 720 Nm<sup>3</sup>. The exhaust gases had a discharge temperature of 240°C. The amount of Nitrogen oxide measured was 1000 ppm, referenced to an imaginary NO<sub>2</sub> content; that means a total of 720 x 1920 mg = 1382.40 g.

1.7 kg of a solution of 30 % H<sub>2</sub>O<sub>2</sub> in water (by weight) was added to the exhaust gas stream before the actual reaction. The solution was atomized into a mist and was continuously injected over the whole exhaust cross-section. This dropped the exhaust gas temperature to about 170-180°C, which was also the temperature in the reactor. 1.67 kg of enriched, technically treated Manganese-dioxide-ore in active form (country of origin = India; 78 % MnO<sub>2</sub> by weight) was used in the reactor. Granulate diameter was between 3 and 8 mm. When the exhaust gases crossed the reactor, the NO<sub>2</sub> content dropped from 1000 ppm to 60 ppm.

#### Example 4

In a further test, exhaust gases produced per example 1 were fed through a reactor 1 as shown in Fig. 1. NO<sub>2</sub>-rich exhaust gases entered the reactor 1 at the bottom through line 2. [? German sentence is grammatically wrong]. A pre-oxidation device 10 was installed in line 2 before the reactor 1 and added the oxidizing media, O<sub>2</sub> in this case. At the top of the reactor 1, a finely ground and distributed mixture of Manganese-dioxide and mineral waste (the undesirable part in an ore as found in nature) was entered into the reactor and was allowed to float down against the flow of the exhaust gases. The solid material was fed into the reactor via a toothed metering/sealing wheel 3 located at the top of the spray tower t [or 1, not clearly readable]. A screw-press 4 fed the metering wheel. [Without seeing figure 1, the "toothed metering/sealing wheel is not fully understandable]. As it slowly floated downwards through the reactor 1, the Manganese-dioxide mixture reacted partially with the NO<sub>2</sub>. A second toothed metering/sealing wheel 6 removed the Manganese-dioxide mixture collected at the bottom 5 of reactor 1 and transported it into a separation (desorption) reactor 7. The mixture in the desorption reactor 7 is heated to a temperature of over 250°C, where the newly formed Manganese nitrates splits again and regenerates back into Manganese-dioxide [beginning with this sentence, the German text changes from the past tense into the present tense, as if this part of the process was not demonstrated in the test]. A suitable line 8 may now return the regenerated Manganese-dioxide back into the reactor 1. The NO<sub>2</sub> released in the desorption reactor may be split into N<sub>2</sub> and O<sub>2</sub> in a catalytic reactor. Should NO<sub>2</sub> be catalytically split into N<sub>2</sub> and O<sub>2</sub>, a small part of CO-containing exhaust gases from a gasoline engine [internal combustion engine] may be used at an elevated temperature, for example 750°C. 10.3 Nm<sup>3</sup> of exhaust gases are required to do this if the exhaust gases contain 4 % CO by volume.

#### Example 5 (see Fig. 2)

Instead of feeding finely ground Manganese-dioxide-ore into reactor 1, a different process may be used. Granulate in the size of 2 - 8 mm made of Manganese-dioxide-ore and mainly containing MnO<sub>2</sub> may slowly tumble downwards over a sieve or similar inside reactor 1. [The writer could not determine, what a "Rieselbett" exactly is. Out of

the context it seems to be a sieve or perforated duct installed under an angle inside the reactor, over which the granulate slowly moves downwards (similar to the oscillating ducts in flour-mills). Fig. 2 might clarify this].

All temperature requirements are as in Example 4. The partially used granulate is being removed at position 6 and transferred into a peeling drum 11. In the peeling drum, sufficient surface material is being removed from the granulates to expose fresh material, ready for renewed reaction. The peeled granulate is fed back to the reactor 1. The material removed in the peeling process is being transported into a desorption reactor and gets regenerated as described in Example 4. After regeneration, the peeled material gets pressed into new granulate (press 12) and is also fed back into reactor 1.

Basically, the peeling process is limited to granulates as used in above "tumble-process".

It should be stressed that in many instances natural Manganese-dioxide-ore contains other components, e.g. iron oxides. Iron oxides too have a catalytic effect; especially the presence of  $\text{Fe}_2\text{O}_3$  can actually improve the effectiveness of  $\text{MnO}_2$ .

#### Patent claims:

1. A process to separate Nitrogen oxides out of exhaust gases from exhaust gases of fired boilers, combustion engines and from other exhaust-gas-producing installations. Exhaust gases are being fed into a reaction chamber filled with solid Manganese-dioxide in an activated state. This Manganese-dioxide will react with at least one of the existing Nitrogen oxides.

The process has the following characteristics:

- Before the exhaust gases react with the Manganese-dioxide, an Oxygen rich media (oxidizer) is being added to the exhaust gases. The two react and Nitrogen-monoxide (NO) is being oxidized to  $\text{NO}_2$ .
- in the reaction occurring afterwards, the temperature is kept at 20 - 200°C. During this time, the original and the newly formed  $\text{NO}_2$  react with the Manganese-dioxide and produce mainly Manganese-nitrate ( $\text{Mn}(\text{NO}_3)_2$ ).

2. A process based on claim 1, identified by the fact that the reaction media containing Manganese-dioxide flows inside the reactor in a crushed form in the same direction or against the exhaust gas flow containing Nitrogen-oxide.

3. A process based on claim 1, identified by the fact that either Oxygen ( $\text{O}_2$ ) or Ozone ( $\text{O}_3$ ) or Hydrogen-peroxide ( $\text{H}_2\text{O}_2$ ) is being used as oxidizing media.

4. A process based on claim 1, identified by the fact that Manganese-dioxide in the form of granulates or pellets with a size of 2 - 8 mm is being used. If found necessary, a small amount of binding agent might be added to the granulates or pellets.

5. A process based on claim 1, 3 or 4, identified by the fact that the Manganese-dioxide

in the reaction media is supplied in the form of a raw ore, that means as a natural, untreated Manganese-dioxide-ore which only has been crushed and ground or formed into granulates or pellets.

6. A process based on claim 5, identified by the fact that the ore containing MnO<sub>2</sub> is ground into a fine dust and is blown directly into the exhaust gas stream to act as the reaction media.

7. A process based on any of the above claims, identified by the fact that Manganese-nitrate, which formed in the reaction process, is being reformed to Manganese-dioxide via thermal separation.

8. A process based on any of the above claims, identified by the fact that the surface of the used [spent] granulate is being peeled until a fresh, active surface appears on the peeled granulate.

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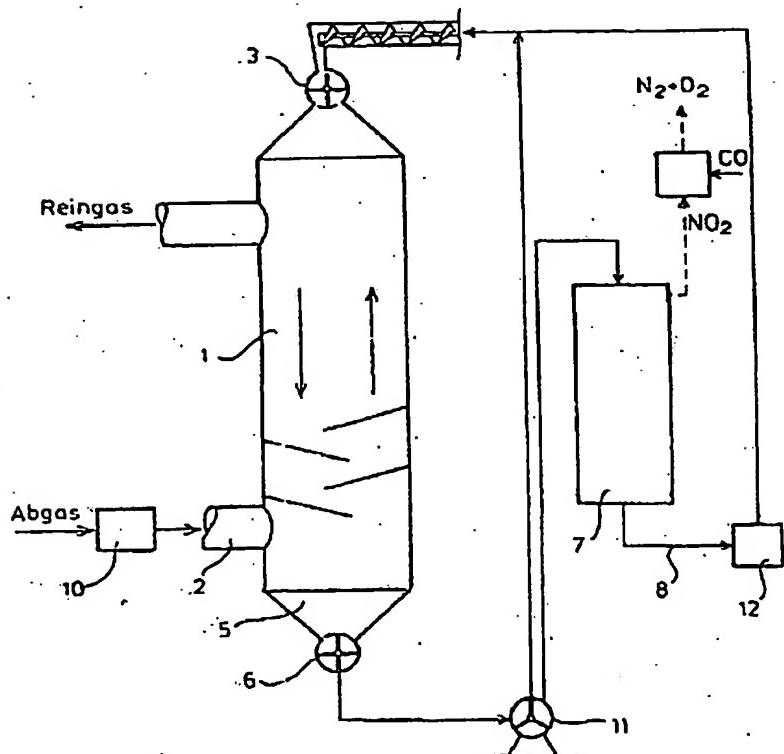


Fig.2

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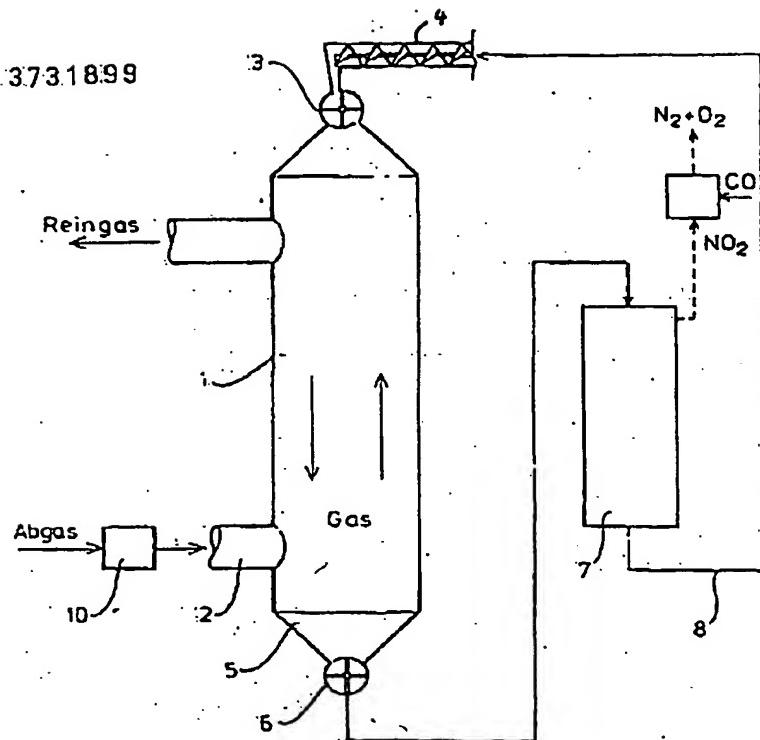


Fig.1

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